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Influences of H on the Adsorption of a Single Ag Atom on Si(111)-7 × 7 Surface

Xiu-Zhu Lin · Jing Li · Qi-Hui Wu

Abstract The adsorption of a single Ag atom on both clear Si(111)-7 × 7 and 19 hydrogen terminated Si(111)-7 × 7 (hereafter referred as 19H-Si(111)-7 × 7) surfaces has been investigated using first-principles calculations. The results indicated that the pre-adsorbed H on Si surface altered the surface electronic properties of Si and influenced the adsorption properties of Ag atom on the H terminated Si surface (e.g., adsorption site and bonding properties). Difference charge density data indicated that covalent bond is formed between adsorbed Ag and H atoms on 19H-Si(111)-7 × 7 surface, which increases the adsorption energy of Ag atom on Si surface.

Keywords Si(111) · H adsorption · Ag adsorption · First-principles calculations

Introduction

Due to both scientific and technological interest, the metal/semiconductor (M/S) interfaces have attracted much attention in order to further advance semiconductor devices and technologies. The current success of the micro- and nano-electronics is made possible by the improvements in the controlled growth of thin layers of semiconductors, metals and dielectrics. The further development of micro- and nano-electronic device technology requires detailed knowledge of the M/S contact formation and thus places new demands on the M/S interfaces. The development of smaller and more complex devices is based on the ability to control these structures down to the atomic level. In this sense, the understanding of the dynamical processes and the local stability of atomic structures on semiconductor surfaces have a significant importance. Among these M/S interfaces, Ag/Si interface has been extensively investigated due to the important applications of Si in the field of semiconductor technology. Moreover, (1) thin Ag film can be used as a model system in the study of two-dimensional (2D) electrical transport phenomena; (2) the Ag/Si system is an example of an abrupt interface with very limited interdiffusion of the two elements and is thus a "prototypical nonreactive" system; and (3) the Ag/Si interface is widely used for contacts and metallization of electronic devices [1–3]. There is a wide range of Si(111) reconstruction surfaces, such as 1 × 1, 2 × 2, 5 × 5 and 7 × 7 as well. Because of the high stability and large unit cell, the adsorption of various metal atoms on Si(111)-7 × 7 surfaces has been extensively studied, for example Au [4, 5], Ge [6], Pd [7], Cu [8], Co [9], In [10], and Zn [11]. Diverse surface science techniques have been applied to study these interfaces, e.g., scanning tunnelling microscopy [12–15], electron energy loss spectroscopy [16], infrared reflecting adsorption spectroscopy [17], photoelectron emission spectroscopy [18] and temperature-programmed desorption [19]. In order to better understand the physical properties of the Ag/Si interfaces, first-principles calculations have also been employed to study these systems [20]. The changes in the atomic and electronic structures of the

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Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface, Ag nanocluster formation on the H-terminated Si(111)-1 × 1 surfaces and diffusion of Ag on the H-terminated Si(111)-1 × 1 and clear Si(111)-1 × 1 surfaces have been studied experimentally and theoretically [20–25]. In present work, we take Ag as an example to investigate the influences of H on the adsorption of metal on the Si(111)-7 × 7 surface using first-principles calculations. H is the main surfactant during the heteroepitaxy of the metals on Si surfaces. When H interacts with Si surface-dangling bonds, this will cause the relaxation of the surface bond strain and reduce the surface free energy [26, 27]. The pre-adsorption of H on Si(111)-7 × 7 will alter the growth mode and morphology of the metal overlayers on the surface [28–30]. It is expected that ideal H-terminated Si single crystal surfaces are generally considered rather unreactive, which will lead to the different surface kinetics and energetics between clean and H-terminated Si(111)-7 × 7 surface.

Calculation Method and Substrate Structures

First-principles calculations within the framework of density functional theory (DFT) were applied to study the influences of H on the adsorption of Ag on the Si(111)-7 × 7 surface using the Vienna ab initio simulation package (VASP) [31]. Ab initio density functional calculations of surfaces and interfaces play a critical role in providing a nanoscopic understanding of the chemical bonding in these systems in the determination of the atomic geometry and electronic structure. A plane-wave method with the Vanderbilt ultrasoft pseudopotentials [32] was used within the spin-independent generalized gradient approximation (GGA) [33] for the exchange-correlation energy. The plane-wave cutoff energy was 200 eV, and the surface Brillouin zone was sampled at the Γ point for the total energy calculations and geometry optimizations. The Si(111)-7 × 7 and 19H-Si(111)-7 × 7 substrate structures were built based on the dimer-adatom-stacking fault (DAS)

model [34]. On the 19H-Si surface, the 19 Si surface dangling bonds (DBs) per unit cell are saturated by H atoms, corresponding to 12 adatoms, six rest atoms and a corner hole of the DAS. The top and side views of these models are shown in Fig. 1. The unit cell contains a slab of five Si layers (200 Si atoms) and a $\sim$12 Å vacuum layer. The bottom of the slab has a bulk-like structure with each Si atom saturated by an H atom. All atoms except for the H and Si atoms at the bottom were fully relaxed to optimize the surface total energy. In this work, the faulted half unit cell (FHUC) was deliberately selected for study because there is little difference in electronic properties between FHUC and unfaulted half unit cell (UHUC) [35, 36] on the Si(111)-7 × 7 surface.

Results and Discussion

To understand the influences of H on the Ag adsorption at a Si(111)-7 × 7 surface, we first calculate the adsorption energies of Ag atom at the high coordination sites on the clear and 19H-Si(111)-7 × 7 surfaces, because all the previous data have confirmed that the high coordination sites on the Si surface are the most favorable adsorption sites for different metal atoms (including Ag) [20, 37]. On account of the symmetry of the three equivalent "basins" in a FHUC, only the adsorption energies at three different high coordination Si surface sites (H_3, B_2 and S) on a "basin" were considered [38]. We derived the adsorption energies from calculating the total energy of the system including full relaxation of all Si atoms and H atoms (except for the bottom hydrogenated Si atoms) and the Ag adatom. The adsorption energies (E_{ad}) are defined as,

$$E_{ad} = E_{sys} - E_{sur} - E_{atom} \tag{1}$$

where E_{sys} is the system energy combining the bonding energy of the Ag adatom on the surface and the surface relaxation energy; E_{sur} is the energy of either Si(111)-7 × 7 or 19H-Si(111)-7 × 7 surfaces, which is

Fig. 1 a The top and side views of dimmer-adatom-stacking (DAS) fault Si(111)-7 × 7 structure. The *blue balls* are the Si adatoms, and the *pink balls* are the Si rest atoms. The positions of H_3, B_2 and S sites are indicated in the *top view* within a "basin", b the top view of 19H-Si(111)-7 × 7 model surface. The small *yellow balls* on the Si atoms with dangling bond are H atoms
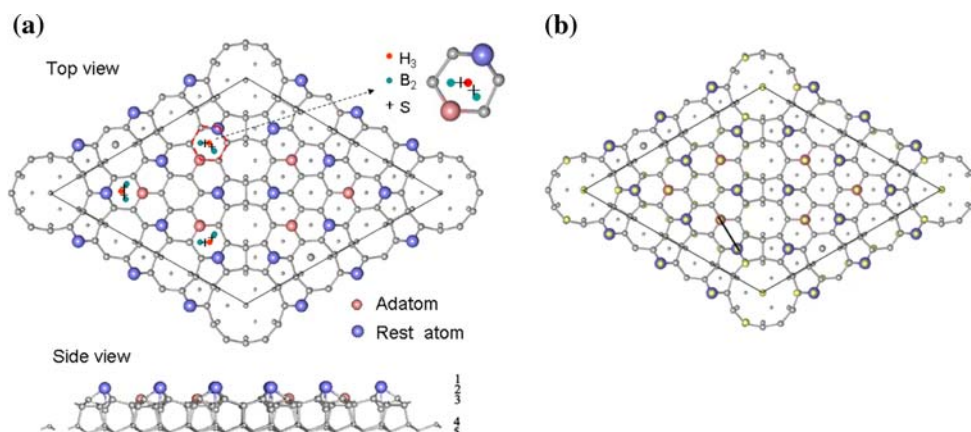
−1,197.073 or −1,278.822 eV, respectively; E_{atom} is the binding energy of one bulk Ag atom , i.e −0.012 eV, and this value is very close to the experimental result [39]. The calculation results show that the most stable site for a single Ag atom adsorption is the S site for clear Si surface, and H_3 site for the 19H-Si(111)-7 × 7 surface. The adsorption energies for Ag atom at the H_3, B_2 and S places on different surfaces are listed in Table 1. The locations of the different sites are indicated in Fig. 1, the S site is almost at the middle between the H_3 and B_2 sites.

The change of the adsorption site of Ag atom because of the pre-adsorption of H on Si(111)-7 × 7 may be due to the reconstruction of Si surface electronic structures induced by H. To depict the charge redistribution associated with the H adsorption on Si(111)-7 × 7 surface in real space, we first calculate the difference charge density after H saturating the 19 surface DBs on the Si(111)-7 × 7

Table 1 The system energy (E_{sys}) and adsorption energy (E_{ad}) of a single Ag atom adsorption on different high coordination sites (H_3, B_2 and S) at Si(111)-7 × 7 and 19H-Si(111)-7 × 7 surfaces

Surface	Site	E_{sys} (eV)	E_{ad} (eV)
Si(111)-7 × 7	H_3	−1,199.384	−2.299
	B_2	−1,199.389	−2.304
	S	−1,199.503	−2.418
19H- Si(111)-7 × 7	H_3	−1,279.740	−0.906
	B_2	−1,279.729	−0.895

The H_3, B_2 and S sites are indicated in Fig. 1

substrate by subtracting the charge densities of the separate Si substrate and H atoms from that of 19H-Si(111)-7 × 7. To verify the differences, the charge densities of the clean Si substrate, 19H-Si(111)- 7 × 7 and isolated H atoms are calculated with the same lattice parameters and atomic positions as the relaxed Ag adsorbed 19H-Si(111)-7 × 7 surface. This allows the charge densities to be easily subtracted point by point in the real space, even for Ag adsorbed surfaces. Figure 2 presents the calculated total valence charge density plots of (a) clean Si substrate, (b) isolated H atoms, (c) H-terminated Si surface in FHUC, and (d) the difference charge density plot. The plot in Fig. 2d is generated by subtracting Fig. 2a, b from c in the plan determined by H atoms, Si adatom and the rest atom in FHUC along the solid line shown in Fig. 1b. In Fig. 2d, the positive contours (solid lines) represent the charge accumulation, whereas the negative contours (dashed lines) represent the charge depletion. The charge density depletes around the H atom and transfer toward the Si adatom when the H sits on the Si adatom. There is a strong covalent bond between the H and the Si rest atom when the H locates on the Si rest atom. These results indicate that due to the strong charge transfer from adsorbed H to the Si adatom, a local positive surface dipole will then form at the Si adatom (H^+-Si^-). This means that H adsorbed on Si adatom has different electronic properties from one adsorbed on the Si rest atom. The calculations also show that the surface atomic charge distribution is much more uniform once all 19 surface DBs have been saturated by H, which is

Fig. 2 Calculated total valence charge density plots of **a** clean Si substrate, **b** isolated H atoms, **c** 19H-Si(111)-7 × 7 and **d** the difference charge density plot by subtracting Fig. 2a and b from c. The area is 11.5 × 8 Å; the contours interval is 0.1e Å⁻³ for Fig. 2a, b and c and 0.5e Å⁻³ for Fig. 2d. Positive contours are shown as *solid lines*, negative contours as *dashed lines* and zero contours have been omitted. *A* is for Si adatom and *R* for Si rest atom, respectively
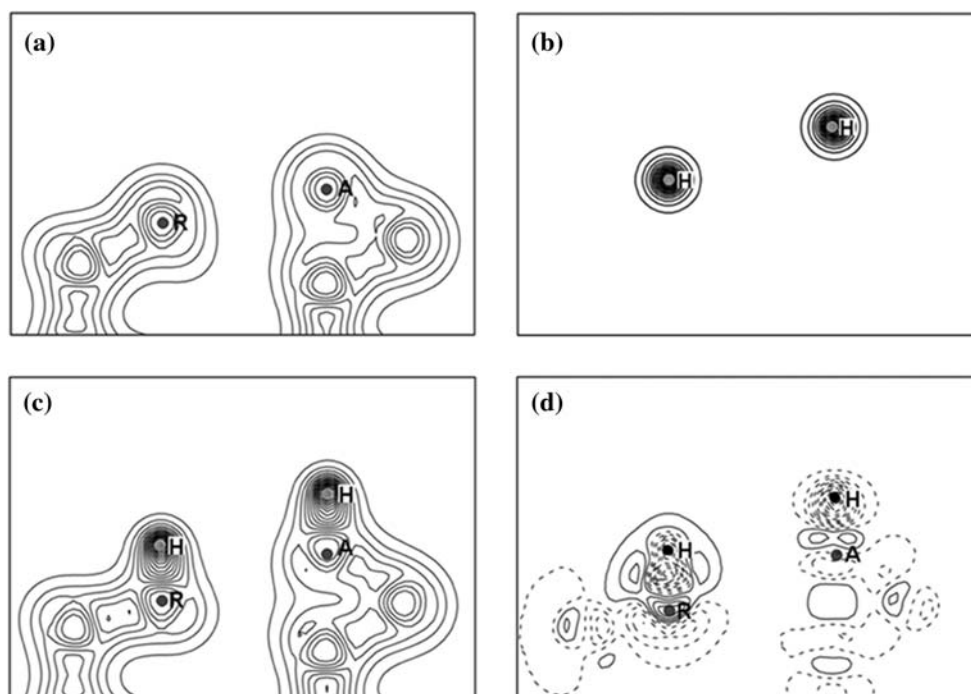
consistent with the previous results reported by Stauffer and Minot [40]. The more uniformity of the surface charge distribution may decrease the Ag diffusion barrier on H-terminated Si(111) surface [20].

By using the same calculation methods, we also obtain the charge distribution associated with the most stable adsorption of Ag at H_3 sites on 19H-Si(111)-7 × 7 surface (in Fig. 3) and the H_3 and S sites on Si(111)-7 × 7 surface (in Fig. 4). Figure 3 shows the total valence charge density plots of (a) the Ag reacted 19H-Si(111)-7 × 7 surface with Ag at the H_3 site in FHUC, (b) isolated Ag atom, and (c) the difference charge density plot. The plot in Fig. 3c is calculated by subtracting Figs. 2c and 3b from Fig. 3a in the plan determined by H atoms, absorbed Ag atom, Si corner adatom and the rest atom. Figure 3c reveals that the charge depletion and accumulation mainly occur between the Ag atom and near H atoms, but no obvious charge difference happens around the close Si atoms. This suggests that after the H passivation, the direct interaction between Ag and Si atoms becomes weak. However, it is interesting to note that the obvious charge accumulation takes place around the third Si atom bonding with Ag at the second layer (not in the plane of Fig. 3c), which has not been adsorbed by H. The charge around the H atom at the Si adatom removes toward the adsorbed Ag atom and forms a covalent-like Ag-H bond. Due to the charge transfer from the H to the Si adatom on the 19H-Si(111)-7 × 7 surface, the H atom is expected to be positively charged. When Ag adsorbs on the surface, charges are much easier to transfer from Ag to this H and form strong covalent bonds. No strong bonding was found between Ag and the H at the Si rest atom.

Figure 4 shows the calculated total valence charge density plots of (a) Ag reacted Si(111)-7 × 7 surface with Ag at the H_3 site in FHUC, (b) isolated Ag atom, (c) the difference charge density plot which is obtained by subtracting Figs. 2a and 4b from Fig. 4a and (d) the difference charge density plot with Ag adsorption at S sites. Without the H atoms on the Si surface, we observe that the charge accumulates around the Ag atom, and strongly depletes around the Si adatom, rest atom and the third adjacent Si atom at the second layer (not in the plane) when Ag adsorbs at H_3 sites on Si(111)-7 × 7 (see in Fig. 4c). These Ag–Si bonds caused by nearly absolute charge diversion are considered as an electrovalent-like bond. However, when Ag adsorbs on the most stable site (S), the charge depletes around Ag atom and transfer toward the Si rest atom and the Si atom at the second layer. It is surprising to find that there is no influence on the charge density around the Si adatom (see in Fig. 4d). Brommer et al. [41] predicted from their principles calculations of a clean Si(111)-7 × 7 surface that nucleophilic species (e.g., Ag), relative to a Si atom, should react with Si-dangling bonds in the order of adatoms, corner holes, and rest atoms. Our results do not support this conclusion.

From above results, one can see that the adsorption behaviors of Ag atom on the Si(111)-7 × 7 and 19H-Si(111)-7 × 7 surfaces are quite different. After passivating the Si surface by H atoms, the adsorbed Ag will form covalent bonds with H atoms at the Si adatom, and
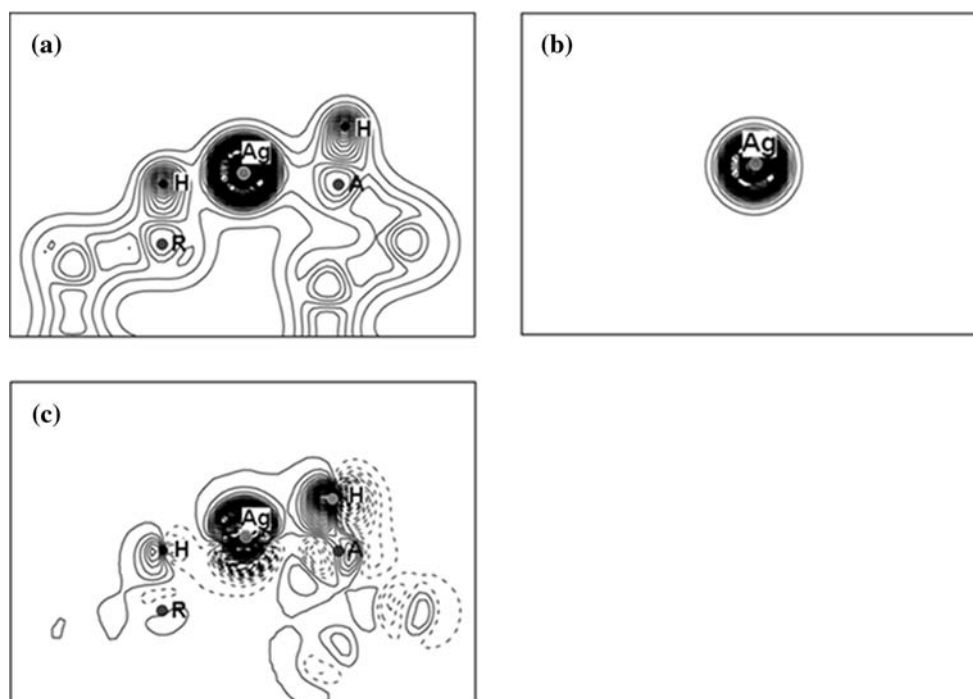
Fig. 3 Calculated total valence charge density plots of: **a** Ag reacted 19H-Si(111)-7 × 7 surface with Ag at the H_3 site, **b** isolated Ag atom and **c** the charge density difference plot by subtracting Figs. 2c and 3b from Fig. 3a. The area is 11.5 × 8 Å, the contours interval is 0.1e Å^{-3} for Fig. 3a and b, and 0.5e Å^{-3} for Fig. 3c

Fig. 4 The calculated total valence charge density plots of **a** Ag reacted Si(111)-7 × 7 surface with Ag at the H_3 site, **b** isolated Ag atom, **c** the difference charge density plot by subtracting Figs. 2a and 4b from Fig. 4a, and **d** the difference charge density plot with Ag at the S site on Si(111)-7 × 7. The area is 11.5 × 8 Å, and the contours interval is 0.1e Å^{-3} for Fig. 4a and b, and 0.02e Å^{-3} for Fig. 4c and d
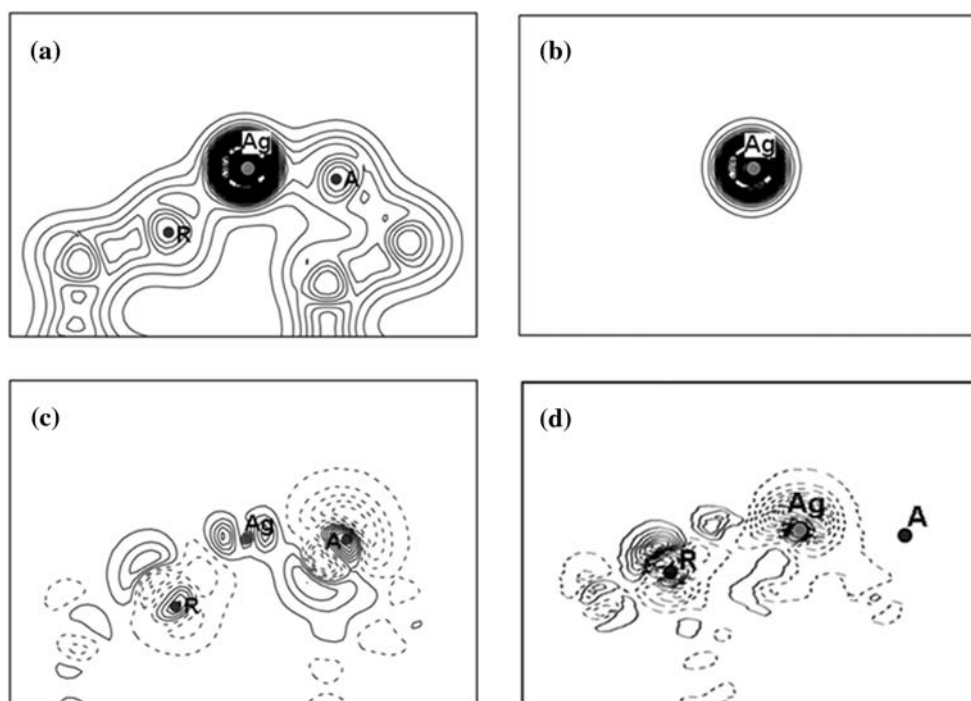
consequently, the interaction between the Ag and the Si atoms become much weaker. Jeong et al. [20] have calculated the diffusion barriers for Ag atom inside the HUCs on the Si(111) and H-terminated Si(111) surfaces, which are 0.14 and 0.27 eV, respectively. The smaller diffusion barrier for Ag atom on the H-terminated Si surface is probably due to the uniformity of the surface atomic charge distribution because of the saturation of the surface Si DBs by H atoms. They further concluded that due to the lower diffusion barrier, three dimension Ag islands would be easily grown on the H-terminated Si(111) surface because all the Si dangling bonds are saturated by H atoms.

Conclusions

The adsorption of a single Ag atom on clear Si(111)-7 × 7 and 19H-Si(111)-7 × 7 surfaces was investigated using first-principles calculations. The results indicated that the adsorption of H atoms at DBs on Si(111)-7 × 7 surface will uniform the surface charge distribution and consequently alter the surface electronic structures. A local surface positive dipole (H^+-Si^-) may form due to the strong charge transfer from H to the Si adatom. When Ag adsorbs at H_3 site on the 19H-Si(111)-7 × 7 surface, a strong covalent bond with the H at the Si adatom was found. The present results provide a theoretic framework for the understanding of the Ag bonding properties on Si(111) and H-terminated Si(111) surfaces.

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